Letters to the Editor

The Board of Editors does not hold itself responsible for opinions expressed in the letters published in this section. The notes containing short reports of original investigations communicated to this section should not contain many figures and should not exceed 500 words in length. The contributions reaching the Secretary by the 15th of any month may be expected to appear in the issue for the next month. No proof will be sent to the author.

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ULTRAVIOLET ABSORPTION OF CHLORATE BROMATE AND IODATE IONS

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Chlorate, bromate and iodate ions are known to have pyramidal structure with C_{3v} symmetry (Herzberg, 1960) in centrast to planar structure with D_{3h} symmetry of nitrate and carbonate ions (Tandon, 1962). Study of electronic structure (Pauling, 1960) of chlorate ion reveals the presence of charge on the chlorine atom, similar to that on nitrogen in nitrate ion (Janz and Mikawa, 1960). The difference in symmetry, structure and charge distribution, demands that the absorption spectrum of chlorate and carbonate ions should not be similar. The ultraviolet absorption spectrum of chlorate bromate and iodate ions has not been studied in details. Consequently, the authors with improved techneque (Tandon, 1961) made a close study of the absorption spectrum of these ions in about ten salts with a UVISPEK spectrophotometer, scanning the spectrum at an interval of 3.5 Å in the region 1850 Å to 3600 Å. Aqueous solutions at different concentrations of the chlorates, bromates and iodates, studied, showed one intense band at about 2000 Å.

The band-width of the band is almost the same for all the three ions and is 10^3 cm^{-1}, which is nearly the same as that of the nitrate ion (Mookherji and Tandon, 1962). Hence it may be inferred that the excited state of the transition giving rise to the band is due to an antibonding orbital. (Jorgensen, 1962).

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The oscillator strength P, which is a measure of the intensity of the band, was calculated following Jorgensen (1954) and Jaffé and Orchin (1962), which comes out 10^{-1} suggesting the band to be due to an allowed transition.

Following Tanabe and Sugano (1954) the transition probabilities were calculated from the P values, which also indicate the transition to be an allowed electronic one.

Constructing molecular orbitals of 26 valence electrons as LCAO appropriate to the C_{3v} point group by the method suggested by McGlynn and Kasha (1956), this may be assigned to the transition which raises an electron from weakly antibonding orbital on oxygen atoms to a strongly antibonding orbital on chlorine, bromine and iodine atoms in chlorate, bromate and iodate ions respectively. The shift of the band towards shorter wavelength (blue shift) coupled with increase with intensity and decrease in band-width with progressive dilution of the aqueous solution exhibits electron transfer spectra characteristics.

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